resulting difference in the free energy of activation between both pathways, $\Delta G^{*}{}_{D} - \Delta G^{*}{}_{I_a}$, will increase considerably as the stability of the adduct increases. This explains why the dissociative pathway is only observed for the less stable adducts of the phosphoryl ligand series. Such a ligand-triggered, dissociative–associative mechanism cross-over has already been observed[39] for ligand exchange on $MX_5{\cdot}L$ adduct ($M = Nb^{5+}$, Ta^{5+}), and a linear free energy relationship with slope of ≈ -1 was found between ΔG^{*} and ΔG° for their dissociative first-order ligand exchange.

It has been shown by vibrational spectroscopy[3] that the $ZrCl_4$ adducts with the dimethyl chalcogenides Me_2Y ($Y = O, S, Se$) exist only in the cis form. Intermolecular exchange of Me_2O on *cis*-$ZrCl_4{\cdot}2Me_2O$ obeys a second-order rate law and has a very negative $\Delta S^{*}{}_{c2}$ value, indicative of an I_a mechanism. The exchange rates on the *cis*-$ZrCl_4{\cdot}2Me_S$ and *cis*-$ZrCl_4{\cdot}2Me_2Se$ adducts were too fast to be measured, probably due to the increase in nucleophilicity of the sulfide and selenide Lewis bases.

In conclusion, intermolecular ligand exchange on the adducts $MCl_{6-n}{\cdot}nL$ ($M = d^0$ transition-metal ion) will obey mechanisms that depend on the nature of the metal M and the exchanging ligand L. Adducts of the second (Nb^{5+}[40] and Zr^{4+}) or third (Ta^{5+}[40] and Hf^{4+}) transition series show a greater tendency toward associative activation modes, whereas adducts of the first transition series (Ti^{4+}[4]) show dissociative activation. Adducts of d^{10} metal ions (Sn^{4+}[7-9] and Sb^{5+}[41]) show the same behavior as Ti^{4+}, i.e. D mechanisms. For the $MCl_4{\cdot}2L$ adducts the cis–trans isomerization is intramolecular, with an expanded transition state for Ti^{4+} and Sn^{4+} and a contracted transition state for Zr^{4+} and Hf^{4+}. Figure 7 illustrates these observations for coordinated–free ligand exchange and cis–trans isomerization on $TiCl_4{\cdot}2(MeO)_3PO$ and $ZrCl_4{\cdot}2(MeO)_3PO$. It exemplifies the striking differences in reaction mechanism due to the increase in ionic radius, which favors the changeover from a dissociative to an associative activation mode.

Acknowledgment. We thank the Swiss National Science Foundation for financial support through Grant No. 2.672-0.87.

Supplementary Material Available: Tables of inverse ligand residence times as a function of free ligand and/or adduct concentration and tables of temperature and/or pressure dependence of the various rate constants (17 pages). Ordering information is given on any current masthead page.

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The Role of One-Parameter Plots in a Two-Parameter World

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Received August 29, 1989

The simplicity of analysis, ease of presentation, and ready extension to new bases (or acids) have led many investigators to choose a one-parameter analysis to interpret physicochemical measurements. Though it is commonly accepted that two factors contribute to donor or acceptor properties, one-parameter correlations often work because much chemistry is dominated by electrostatic interactions. An improved set of enthalpy-based parameters are presented for such analyses as alternatives to donor numbers, Kamlet–Taft β values, and pK_B data. The conditions that must apply in order for a one-parameter analysis to be valid are described, and criteria are offered to indicate when a one-parameter analysis can be misleading. It is shown that an improper estimate of the covalency in a physicochemical measurement relative to that in the basicity scale utilized can lead to deviations in plotted data which could lead an investigator to improperly conclude that steric effects or metal to ligand π-back-bonding exists.

Introduction

In 1965, we published[1] an analysis of the solution enthalpies for reactions of donors with acceptors to form 1:1 adducts in nonpolar, nonbasic solvents, where solvation contributions are minimal. A one-term equation cannot possibly accommodate even the limited data set which indicates a donor order toward iodine of $R_3N > R_2S > R_2O$ and one toward phenol of $R_3N > R_2O > R_2S$. A two-term E and C (electrostatic and covalent) equation was found[1,2] to be sufficient for the correlation of these as well as over 500 other enthalpies of adduct formation.

$$-\Delta H = E_A E_B + C_A C_B - W \qquad (1)$$

Empirical E_A, E_B, C_A, C_B, and W parameters are reported[3] for the acids and bases to correlate these enthalpies. W represents a constant contribution to the enthalpy; W for an acid is independent of the base employed. The essential conclusion of this treatment is that there is no single reference acid (or base) that can lead to reference parameters that provide an inherent order of basicity (or acidity). For example, it was shown[4] that the Kamlet–Taft β parameters[5] are a special case of the E and C equation that applies to mainly electrostatic acids or acid properties. They fail to correlate systems with more appreciable covalent contributions.

The various donor orders that can result for a series of bases as the type of acid varies can be illustrated by factoring and rearranging eq 1 as described by Cramer and Bopp:[6]

$$\frac{-\Delta H + W}{C_A + E_A} = \frac{C_B + E_B}{2} + \left(\frac{C_B - E_B}{2}\right)\left(\frac{C_A - E_A}{E_A + C_A}\right) \qquad (2)$$

With use of the reported E and C parameters, the graph in Figure 1 can be constructed as described in ref 7. Different acids are

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(7) The $-\Delta H$ value for a selected base reacting with phenol is calculated from eq 1 by using reported E and C parameters. $-\Delta H$ divided by $C_A + E_A$ is plotted on a graph of $-\Delta H/(C_A + E_A)$ vs $(C_A - E_A)/(C_A + E_A)$. The enthalpy is then calculated with reported parameters for the same base reacting with I_2, the point plotted, and a straight line drawn connecting the points. Equation 2 is that of a straight line, and the calculated enthalpies for all acids interacting with this base will fall on this line. The procedure is repeated for a series of bases diethyl sulfide (51), diethyl ether (40), pyridine (16), N-methylimidazole (15), and dimethyl sulfoxide (56), and the resulting plot is shown in Figure 1. (The numerical values in parentheses correspond to the base-numbering scheme in Table I.)

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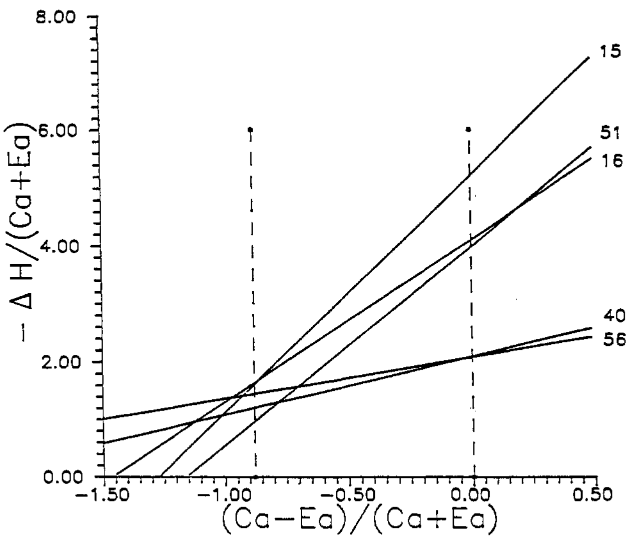

Figure 1. E and C representation of the various donor orders for representative Lewis bases. (The numbering corresponds to that in Table I.)

located along the horizontal axis depending upon their value of $(C_A - E_A)/(E_A + C_A)$. The donor order for each acid can be read off from the $-\Delta H/(C_A + E_A)$ value for each point. The dashed line at the x coordinate value of 0.00 corresponds to I_2 [$(C_A - E_A)/(E_A + C_A)$ equals zero when $C_A = 1$ and $E_A = 1$ for I_2] and leads to a donor order N-Meimid > py ~ Et_2S > Et_2O ~ $(CH_3)_2SO$. The dashed line at −0.88 represents phenol, and this acid produces a donor order py ~ N-Meimid > $(CH_3)_2SO$ > Et_2O > Et_2S. Every time two lines cross, the donor order for acids on either side of the intersection reverses. With all the intersections shown in Figure 1, a multitude of donor orders of σ-bond strength results for these five bases as the acid is changed. This graph illustrates the futility of attempting to find a reference acid to provide a universal order of donor strength.

The need for at least a two-term approach to correlate and understand chemical reactivity is now a generally accepted conclusion.[8-10] The greater complexity of analyzing and presenting data with a two-term model as opposed to analyzing data with the linear plots of a one-term approach has led to the continued appearance of one-term plots and analyses. It is common to find a quantitative measure of some phenomenon plotted vs pK_B's and deviations from the plots rationalized with electronic arguments. The purpose of this article is to indicate when the one-term approach is valid, to present enthalpy-based parameters for a one-term approach that are more meaningful than pK_B's or β parameters,[5] and to illustrate the consequences of incorrectly using a one-term approach.

Results and Discussion

Conditions for One-Term Correlations. This discussion will be presented in terms of measuring some property of a system that varies as the base involved in the interaction is changed. The arguments are general, and the word acid could be interchanged for base if the acid were being varied. The objective of the analysis is to determine if the observed trends in the measured property are brought about by changes in the donor strength of the base. The *ECW* equation can be used to determine if a change in a measured physicochemical property, $\Delta\chi$, correlates with the two effects (covalency and electrostatic) involved in base σ-donor strength. The measured property is substituted for $-\Delta H$ in eq 1, and the change in the property is measured for a series of bases whose E_B and C_B numbers are known. The simultaneous equations (one for each base studied) of the form

$$\Delta\chi + W = E_A{}^*E_B + C_A{}^*C_B \qquad (3)$$

are then solved for $E_A{}^*$, $C_A{}^*$, and W. The asterisk indicates that these E_A and C_A parameters are not enthalpy based. Since $-\Delta H$ in eq 1 has units of kcal mol^{-1}, E_B and C_B have units of (kcal mol^{-1})$^{1/2}$. Thus, $E_A{}^*$ and $C_A{}^*$ have units to convert $E_A{}^*E_B$ and $C_A{}^*C_B$ to the units of $\Delta\chi$. The enthalpy-based E_B and C_B parameters are used as the criterion of donor strength, and the analysis described above for $C_A{}^*$ and $E_A{}^*$ permits the electrostatic and covalent properties of the donor ($E_A{}^*E_B$ and $C_A{}^*C_B$) to be weighted differently in their contribution to $\Delta\chi$ than they are to $-\Delta H$. This is not the case if $-\Delta\chi$ is plotted vs ΔH.

If one is dealing with properties whose C_A/E_A ratio is constant, it is possible to convert eq 3 to a one-term equation.[11] Dividing both sides of eq 3 by E_A produces

$$\frac{\Delta\chi + W}{E_A} = \frac{C_A}{E_A}C_B + E_B \qquad (4)$$

With C_A/E_A constant, the right-hand side of the equation becomes a constant, B_c, for each given base.

$$B_c = \frac{C_A}{E_A}C_B + E_B \qquad (5)$$

The subscript c indicates the C_A/E_A ratio of the two-term equation for which this one parameter treatment is valid. One-parameter, enthalpy-based, donor orders have been generated (B_c) for acids with a fixed C_A/E_A ratio, vide infra.

Substituting the expression for B_c (eq 5) into eq 4 produces

$$\Delta\chi + W = B_cE_A \qquad (6)$$

Thus, $\Delta\chi$ can be plotted vs these B_c parameters to give a straight line with slope E_A and intercept $-W$ when the measured property has the same $C_A{}^*/E_A{}^*$ ratio as that for which B_c is calculated. A good linear correlation for σ-donors indicates that $\Delta\chi$ is dominated by σ-donor bond strength, and deviations from the plot for other donors indicate unusual electronic effects. The problem is that one does not know what the $C_A{}^*/E_A{}^*$ ratio of a given acid for $\Delta\chi$ is, so one does not know which B_c parameters to use.

Some One-Term Parameters. A common C/E ratio for a large number of chemical interactions and spectroscopic trends (i.e. $\Delta\chi$'s) is found to be 0.01. This ratio correlates electronic spectral hydrogen-bonding shifts,[4] free energies of bases hydrogen bonding to alcohols, ^{19}F NMR shifts of acids hydrogen bonding to bases,[12] and the pk_B's of several bases.[4] The corresponding base parameters that can be used to plot this type of data are listed in Table I as $B_{0.01}$ parameters. These parameters are calculated from the E and C equation by using

$$B_{0.01} = E_B + 0.01C_B \qquad (7)$$

One can add new bases to this list by a simple NMR measurement as shown in ref 13. The ready extension of the $B_{0.01}$ parameters to new bases by a simple ^{19}F NMR measurement constitutes the main justification for considering a one-term correlation.

Another commonly encountered C_A/E_A ratio for measured physicochemical properties is 0.1. The measured enthalpies of base hydrogen bonding to alcohols and the changes in the OH stretching frequency shift, $\Delta\nu_{OH}$, of phenol and substituted phenols when they hydrogen bond ($\Delta\nu_{OH} = \nu_{OH} - \nu_{ROH\cdots B}$) have C/E ratios

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(13) Tentative $B_{0.01}$ parameters can be obtained from the difference in shift of the ^{19}F resonance of the 4-fluorophenol[12] base adduct and that of the uncomplexed phenol in CCl_4 solvent. Equation 8 relates the reported values for the change in the ^{19}F NMR peak upon hydrogen bonding to a series of bases to the $B_{0.01}$ parameter. This equation results via substitution of $\Delta\delta$ for $\Delta\chi$ in eq 6.

$$\Delta\delta(^{19}\mathrm{F}) = 2.06B_{0.01} - 0.066 \qquad (8)$$

Table I

Enthalpy-Based $B_{0.01}$ and $B_{0.1}$ Values To Describe Donor Strengths toward Electrostatic Acids (C/E = 0.01 and 0.10, Respectively)

no.	base	$B_{0.1}$	$B_{0.01}$[a]	no.	base	$B_{0.1}$	$B_{0.01}$
1	NH_3	1.81	1.52	42	$(C_4H_9)_2O$	1.45	1.17
2	CH_3NH_2	2.06	1.57	43	$O(CH_2CH_2)_2O$	1.31	1.10 (0.94)[a]
3	$(CH_3)_2NH$	2.18	1.44	44	$(CH_2)_4O$	1.49	1.11
4	$(CH_3)_3N$	2.31	1.33	45	$(CH_2)_5O$	1.45	1.12
5	$(C_2H_5)NH_2$	2.11	1.58	46	$(CH_3)_2O$	1.37	1.12
6	$(C_2H_5)_2NH$	1.97	1.22	47	$(nC_8H_{17})_2O$	1.47	1.15
7	$(C_2H_5)_3N$	2.37	1.43	48	$C_6H_{10}O$	1.35	1.01
8	$C_5H_{11}N$	2.18	1.39				
9	$HC(C_2H_4)_3N$	2.61	1.30	50	$(CH_3)_2S$	1.29	0.660
				51	$(C_2H_5)_2S$	1.29	0.643
15	CH_3im	2.05	1.29	52	$(CH_2)_3S$	1.22	0.652
16	C_5H_5N	1.96	1.38	53	$(CH_2)_4S$	1.29	0.677
17	$4\text{-}CH_3C_5H_4N$	2.04	1.39	54	$(CH_2)_5S$	1.31	0.681
18	$3\text{-}CH_3C_5H_4N$	1.99	1.38				
19	$4\text{-}CH_3OC_5H_4N$	2.03	1.41	56	$(CH_3)_2SO$	1.64	1.40
20	$3\text{-}ClC_5H_4N$	1.74	1.29	57	$(CH_2)_4SO$	1.71	1.49
21	$3\text{-}CF_3C_5H_4N$	1.69	1.26				
22	$4\text{-}CNC_5H_7N$	1.53	1.19	60	C_5H_5NO	1.84	1.45
23	$3\text{-}CNC_5H_4N$	1.58	1.21	61	$4\text{-}CH_3C_5H_4NO$	1.93	1.50
				62	$4\text{-}CH_3OC_5H_4NO$	2.07	1.57
25	CH_3CN	1.03	0.917	63	$C_9H_{18}NO$	0.68	1.16
26	$ClCH_2CN$	0.93	0.878				
27	$(CH_3)_2NCN$	1.23	1.08	65	$[(CH_3)_2N]_3PO$	1.88	1.64
				66	$(C_2H_5)_3PO_4$	1.55	1.39
30	$CH_3C(O)CH_3$	1.24	1.04				
31	$CH_3C(O)OCH_3$	1.10	0.942	70	$(CH_3)_3P$	1.76	1.19
32	$CH_3C(O)OC_2H_5$	1.11	0.943	71	$C_2H_5C(CH_2O)_3P$	1.38	0.812
33	$CH_3C(O)N(CH_3)_2$	1.57	1.35				
34	$HC(O)N(CH_3)_2$	1.49	1.27	75	$(CH_3)_2Se$	1.29	0.591
				76	C_6H_6	0.49	0.411
40	$(C_2H_5)_2O$	1.39	1.12				
41	$(C_3H_7)_2O$	1.47	1.20				

Spectral-Based $B_{0.1}$ Values and Values from $\Delta\nu_{OH}$ and β Parameters

no.	base	$B_{0.1}$	$B_{0.01}$	no.	base	$B_{0.1}$	$B_{0.01}$
100	$(C_6H_5)_3PO$	1.87	1.66	109	$CH_3O(CH_2)_2OCH_3$	1.33	0.99
101	$(CH_3)_3PO$	1.96	1.76	110	quinoline	2.09	1.28
102	$\underline{O(CH_2)_3C}{=}O$	1.18	1.09	111	$(CH_2)_5CO$	1.34	1.14
				112	$(C_6H_5O)_3PO$		1.25
103	$CH_3\underline{N(CH_2)_3C}{=}O$	1.60	1.44	113	C_2H_5OH[b]	1.35	1.03
104	$HC(O)OC_2H_5$		0.925	114	CH_3OH[b]	1.33	0.99
105	$C_6H_5C(O)CH_3$	1.22	1.09	115	H_2O[b]	1.17	0.95
106	C_6H_5CHO	1.15	1.03	116	C_6H_5OH[b]		0.75
107	$CO[N(CH_3)_2]_2$	1.63	1.45	117	$(CH_3)_3COH$	1.41	1.09
108	$CO(OCH_3)_2$		0.95				

[a] Based on spectral shifts. [b] Behaving as bases. (Laurence, C.; Berthelot, M.; Helbert, M.; Sraidi, K. *J. Phys. Chem.* **1989**, *93*, 3799.)

of 0.07 and 0.11, respectively. The donor number scale is based on $SbCl_5$ enthalpies measured in 1,2-dichloroethane.[14] The corrected enthalpies[7] for this scale give a reasonable fit to E_A = 17.5 and C_A = 1.54 with a C/E ratio of 0.07.[15] The enthalpies of coordination of BF_3 to donors measured in CH_2Cl_2 solvent have been proposed[9b] as a scale of donor strength. An E and C analysis yields a C/E ratio of 0.1 for BF_3 after the enthalpies are corrected[16] for the base hydrogen bonding to CH_2Cl_2. The corresponding $B_{0.1}$ parameters, which can replace all these other scales, for a one-parameter fit of physicochemical data are also contained in Table I. Measurement of the infrared frequency shift of phenol, $\Delta\nu_{OH}$, for a new Lewis base enables one to obtain a tentative $B_{0.1}$ parameter with the equation

$$B_{0.1} = \frac{\Delta\nu_{OH} + W}{E_A{}^*} \qquad (9)$$

where $E_A{}^*$ = 334 and W = 205 for phenol. Values for other alcohols are reported in the literature.[3]

The ready extension of these one-parameter scales to new bases by carrying out simple spectral measurements is their main advantage. To obtain a set of tentative E_B and C_B values, the minimum of an IR hydrogen bond shift and an enthalpy of adduct formation with an acid with a C/E ratio >0.3 must be measured.[2] Unfortunately, no spectroscopic correlations with a C_A/E_A ratio >0.2 have been established. If one existed, tentative C_B and E_B values could be obtained by spectroscopy. In contrast, the $B_{0.01}$ and $B_{0.1}$ values are readily obtained from spectroscopic studies as described above. Since many physicochemical properties are mainly electrostatic (the $C^*/E_A{}^*$ ratio is in the range 0.01–0.12), one-term correlations with the $B_{0.01}$ or $B_{0.1}$ parameters will often work.

Pitfalls in One-Term Correlations. Problems arise with a one-term correlation when the C/E ratio of the physicochemical property does not match the C/E ratio of the parameter against which the property is plotted. Misinterpretation of the chemistry often results. The pitfalls are illustrated by generating a synthetic set of $\Delta\chi$ values from eq 6 by multiplying $B_{0.1}$ and $B_{0.01}$ by an E_A value of 2.0 with W = 0. The resulting data is labeled $\Delta\chi_{0.1}$ and $\Delta\chi_{0.01}$, respectively. The synthetic data eliminate possible complications to this analysis from experimental error. When

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(14) Gutmann, V. *The Donor Acceptor Approach to Molecular Interaction*; Plenum: New York, 1978.

(15) Depending on the intercept shown at zero $-\Delta H$, the $SbCl_5$ data can be fit to either $B_{0.1}$ or $B_{0.01}$.

(16) Drago, R. S.; Nusz, J. A.; Courtright, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 2802. The new parameters[3] for E and C require new parameters for the hydrogen bonding correction in CH_2Cl_2 to E' = 1.71 and C' = −0.04.

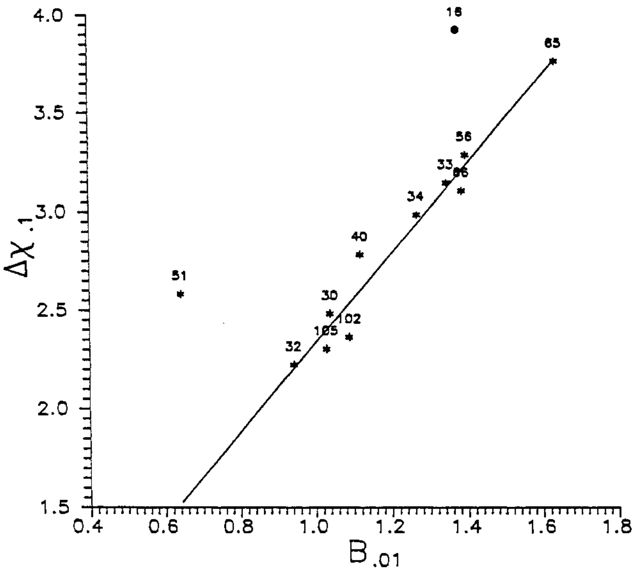

Figure 2. Plot of a physicochemical property with a C/E ratio of 0.1 versus the $B_{0.01}$ parameter whose C/E ratio is 0.01.

$\Delta\chi_{0.01}$ is plotted vs $B_{0.01}$ or $\Delta\chi_{0.1}$ vs $B_{0.1}$, a straight line must result. In Figure 2, the value of $\Delta\chi_{0.1}$ is plotted versus the $B_{0.01}$ parameters. First, consider the points represented by the bases acetone (30), ethyl acetate (32), DMA (33), DMF (34), diethyl ether (40), dimethyl sulfoxide (56), triethyl phosphate (66), butyrolactone (102), acetophenone (105), and hexamethylphosphoramide (65). A very good fit to the incorrect $B_{0.01}$ parameter results. If, as is often done in the literature,[5,8] the correlation coefficient is used to support the interpretation, a linear correlation ($y = 2.24x + 0.088$) results with a value of $r = 0.98$ with $n = 10$ for the 10 bases even though we know the correlation with $B_{0.01}$ is incorrect and the correct one involves $B_{0.1}$. Points based on the donors in Table I numbered 62, 61, 60, 57, 48, 47, 46, 45, 43, 42, 41, 31, 27, 26, and 25 would also fit well, raising the n value to an impressive 25. The statistical analysis is shown to be meaningless when amines, pyridines, or sulfur donors are added to the data fit and the true picture evolves. The pyridine (16) and diethyl sulfide (51) points miss badly and show that the correlation with the $B_{0.01}$ parameters is not valid because they underestimate the covalency in the interaction. Unfortunately, many of the reported one-term sets of parameters for base strength do not include sulfur, amine, or pyridine donors. The donors that fall on the line in Figure 2 all have C_B/E_B ratios of ~2–4. The true nature of the acid property is determined when donors with a wide ratio of C_B/E_B are employed. Hence, correlations must be judged by the variation in the C_B/E_B ratio of the donors used, in addition to the correlation coefficient. It is to be emphasized that the $B_{0.01}$ and $B_{0.1}$ parameters both describe systems in which the interaction is largely electrostatic so the difference in the data set and the reference parameters is not exaggerated. Differences would be substantial with a set of $\Delta\chi_{0.5}$ data (using $C_A{}^* = 0.5$ and $E_A{}^* = 1$ in eq 3 to calculate $\Delta\chi$) plotted vs $B_{0.01}$.

The plot shown in Figure 2 bears a resemblance to literature plots of physicochemical properties of a transition metal or organometallic system versus the pK_B of the donor. In such systems it is common to see the deviant points rationalized by extra stabilization from π back-bonding. With pK_B often paralleling $B_{0.01}$, plotting a transition-metal property, in which the pK_B underestimates the effects of covalency in the interaction, will lead to the same deviations as in Figure 2. In a system where π-back-bonding is a possibility, acetonitrile and *N*-methylimidazole (or a tertiary amine) should be included in the bases studied. Acetonitrile will fall on the line for a $\Delta\chi_{0.1}$ vs $B_{0.01}$ plot but should fall off the line if π-back-bonding really exists. On the other hand, imidazole will fall on the line if π-back-bonding exists and the system is truly characterized by $\Delta\chi_{0.01}$ but will fall off the line if covalency is improperly represented in the parameters employed. Without proper donor selection, an invalid assessment of the important electronic factors involved in a physicochemical measurement is possible.

One may inquire at this point why $B_{0.2}$, $B_{0.3}$, etc. parameters are not reported. Such systems are rare. If a new system were encountered with $C/E \geq 0.2$, one could readily determine B_n parameters from

$$B_n = E_B + nC_B \tag{10}$$

to plot versus this property.

In conclusion, one-parameter scales, $B_{0.01}$ and $B_{0.1}$, are reported that are enthalpy based and thus provide greatly improved scales of σ-donor strength compared to pK_B, donor numbers,[13] β,[5] etc. Simple spectroscopic measurements are described that permit an extension of the parameters to new bases. Finally, the importance of proper donor selection in the design of the experiment is shown and the importance of the C_B/E_B ratio is shown to be an important criterion for the reexamination of conclusions reported in the literature from one-parameter correlations with impressive correlation coefficients.

Acknowledgment. I wish to acknowledge funding for this research by the National Science Foundation through Grant No. 86 18766.